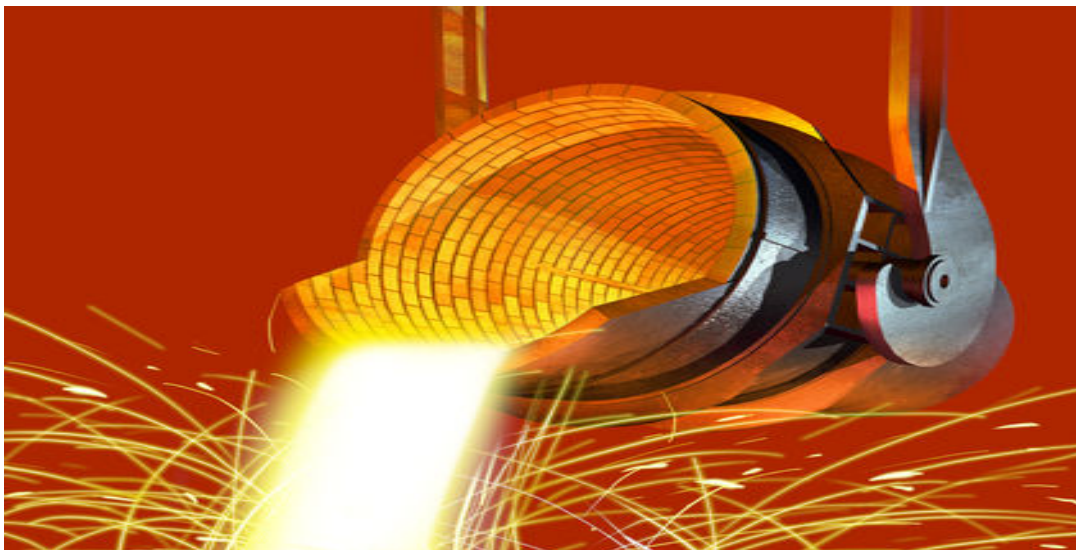




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## CLEANER PRODUCTION GUIDELINES IN COPPER SMELTING INDUSTRIES



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## COPPER SMELTING

Copper can be produced either pyro-metallurgically or hydro-metallurgically. The hydrometallurgical route is used only for a very limited amount of the world's copper production and is normally only considered in connection with in-situ leaching of copper ores; from an environmental point of view, this is a questionable production route. Several different processes can be used for copper production.

The traditional process is based on roasting, smelting in reverberatory furnaces (or electric furnaces for more complex ores), producing matte (copper-iron sulfide), and converting for production of blister copper, which is further refined to cathode copper. This route for production of cathode copper requires large amounts of energy per ton of copper: 30–40 million British thermal units (btu) per ton cathode copper. It also produces furnace gases with low sulfur dioxide (SO<sub>2</sub>) concentrations from which the production of sulfuric acid or other products is less efficient.

The sulfur dioxide concentration in the exhaust gas from a reverberatory furnace is about 0.5–1.5%; that from an electric furnace is about 2–4%. So-called flash smelting techniques have therefore been developed that utilize the energy released during oxidation of the sulfur in the ore. The flash techniques reduce the energy demand to about 20 million Btu/ton of produced cathode copper. The SO<sub>2</sub> concentration in the off gases from flash furnaces is also higher, over 30%, and is less expensive to convert to sulfuric acid. (Note that the INCO process results in 80% sulfur dioxide in the off gas.) Flash processes have been in use since the 1950s.

In addition to the above processes, there are a number of newer processes such as Noranda, Mitsubishi, and Contop, which replace roasting, smelting, and converting, or processes such as ISA-SMELT and KIVCET, which replace roasting and smelting. For converting, the Pierce-Smith and Hoboken converters are the most common processes.

The matte from the furnace is charged to converters, where the molten material is oxidized in the presence of air to remove the iron and sulfur impurities (as converter slag) and to form blister copper.

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Blister copper is further refined as either fire refined copper or anode copper (99.5% pure copper), which is used in subsequent electrolytic refining. In fire refining, molten blister copper is placed in a fire-refining furnace, a flux may be added, and air is blown through the molten mixture to remove residual sulfur. Air blowing results in residual oxygen, which is removed by the addition of natural gas, propane, ammonia, or wood. The fire-refined copper is cast into anodes for further refining by electrolytic processes or is cast into shapes for sale.

In the most common hydrometallurgical process, the ore is leached with ammonia or sulfuric acid to extract the copper. These processes can operate at atmospheric pressure or as pressure leach circuits. Copper is recovered from solution by electro winning, a process similar to electrolytic refining. The process is most commonly used for leaching low-grade deposits in situ or as heaps.

Recovery of copper metal and alloys from copper-bearing scrap metal and smelting residues requires preparation of the scrap (e.g., removal of insulation) prior to feeding into the primary process. Electric arc furnaces using scrap as feed are also common.

### **Waste Characteristics**

The principal air pollutants emitted from the processes are sulfur dioxide and particulate matter. The amount of sulfur dioxide released depends on the characteristics of the ore—complex ores may contain lead, zinc, nickel, and other metals— and on whether facilities are in place for capturing and converting the sulfur dioxide. SO<sub>2</sub> emissions may range from less than 4 kilograms per metric ton (kg/t) of copper to 2,000 kg/t of copper. Particulate emissions can range from 0.1 kg/t of copper to as high as 20 kg/t of copper.

Fugitive emissions occur at furnace openings and from launders, casting molds, and ladles carrying molten materials. Additional fugitive particulate emissions occur from materials handling and transport of ores and concentrates.

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Some vapors, such as arsine, are produced in hydrometallurgy and various refining processes. Dioxins can be formed from plastic and other organic material when scrap is melted. The principal constituents of the particulate matter are copper and iron oxides. Other copper and iron compounds, as well as sulfides, sulfates, oxides, chlorides, and fluorides of arsenic, antimony, cadmium, lead, mercury, and zinc, may also be present. Mercury can also be present in metallic form. At higher temperatures, mercury and arsenic could be present in vapor form. Leaching processes will generate acid vapors, while fire refining processes result in copper and SO<sub>2</sub> emissions. Emissions of arsine, hydrogen vapors, and acid mists are associated with electro-refining.

Wastewater from primary copper production contains dissolved and suspended solids that may include concentrations of copper, lead, cadmium, zinc, arsenic, and mercury and residues from mold release agents (lime or aluminum oxides). Fluoride may also be present, and the effluent may have a low pH. Normally there is no liquid effluent from the smelter other than cooling water; wastewaters do originate in scrubbers (if used), wet electrostatic precipitators, cooling of copper cathodes, and so on. In the electrolytic refining process, by-products such as gold and silver are collected as slimes that are subsequently recovered. Sources of wastewater include spent electrolytic baths, slimes recovery, spent acid from hydrometallurgy processes, cooling water, air scrubbers, wash downs, storm water, and sludges from wastewater treatment processes that require reuse/recovery or appropriate disposal.

The main portion of the solid waste is discarded slag from the smelter. Discard slag may contain 0.5–0.7% copper and is frequently used as construction material or for sandblasting. Leaching processes produce residues, while effluent treatment results in sludges, which can be sent for metals recovery. The smelting process typically produces less than 3 tons of solid waste per ton of copper produced.

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## **Pollution Prevention and Control**

Process gas streams containing sulfur dioxide are processed to produce sulfuric acid, liquid sulfur dioxide, or sulfur. The smelting furnace will generate process gas streams with SO<sub>2</sub> concentrations ranging from 0.5% to 80%, depending on the process used. It is important, therefore, that a process be selected that uses oxygen-enriched air (or pure oxygen) to raise the SO<sub>2</sub> content of the process gas stream and reduce the total volume of the stream, thus permitting efficient fixation of sulfur dioxide. Processes should be operated to maximize the concentration of the sulfur dioxide. An added benefit is the reduction of nitrogen oxides (NO<sub>x</sub>). Closed-loop electrolysis plants will contribute to prevention of pollution. Continuous casting machines should be used for cathode production to avoid the need for mold release agents. Furnaces should be enclosed to reduce fugitive emissions, and dust from dust control equipment should be returned to the process.

Energy efficiency measures (such as waste heat recovery from process gases) should be applied to reduce fuel usage and associated emissions. Recycling should be practiced for cooling water, condensates, rainwater, and excess process water used for washing, dust control, gas scrubbing, and other process applications where water quality is not a concern. Good housekeeping practices are key to minimizing losses and preventing fugitive emissions. Such losses and emissions are minimized by enclosed buildings, covered or enclosed conveyors and transfer points, and dust collection equipment. Yards should be paved and runoff water routed to settling ponds. Regular sweeping of yards and indoor storage or coverage of concentrates and other raw materials also reduces materials losses and emissions.

## **Treatment Technologies**

Fabric filters are used to control particulate emissions. Dust that is captured but not recycled will need to be disposed of in a secure landfill or other acceptable manner. Vapors of arsenic and mercury present at high gas temperatures are condensed by gas cooling and removed. Additional scrubbing may be required. Effluent treatment by precipitation, filtration, and so on of process bleed streams, filter backwash waters, boiler blow down, and other streams may be required to

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reduce suspended and dissolved solids and heavy metals. Residues that result from treatment are sent for metals recovery or to sedimentation basins. Storm waters should be treated for suspended solids and heavy metals reduction. Slag should be land filled or granulated and sold. Modern plants using good industrial practices should set as targets total dust releases of 0.5–1.0 kg/t of copper and SO<sub>2</sub> discharges of 25 kg/t of copper. A double-contact, double-absorption plant should emit no more than 0.2 kg of sulfur dioxide per ton of sulfuric acid produced (based on a conversion efficiency of 99.7%).

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